IRON-MANGANESE-SILICON-BASED SHAPE MEMORY ALLOYS CONTAINING CHROMIUM AND NITROGEN

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a shape memory alloys. In particular, it relates to iron-manganese-silicon-based shape memory alloys containing Cr and N, and training method therefor.

[0002] Shape memory alloys are metallic materials that, when deformed, have the ability to recover their previous shape or size when exposed to a thermal procedure. There are generally two types of shape memory alloys: those that demonstrate shape memory from deformed martensite to austenite only upon heating ("one-way" shape memory alloys); and those that demonstrate a first shape memory when heated and a second memory in an opposite way to deformed martensite when cooled ("two-way" shape memory alloys). Basically, when the shape memory alloy article is cold (or below its transformation temperature), it can be readily bent from its original first shape to a new second shape. However, when heated to a point above its transformation temperature, the article will return to its first shape as a result of a change in crystal structure.

[0003] A variety of shape memory alloys are known in the art. Since the discovery of memory effects in iron-based single-crystal Fe (30) – Mn (1) - Si alloys, a variety of iron-based shape memory alloys have been developed. For example, Chinese Patent Publication CN1064507A discloses a Fe-Mn-Si shape memory alloy having Cr, C,

Ni, and, optionally, Al or N. However, many such alloys require in excess of three training cycles in order to achieve satisfactory shape memory effect. This requirement causes significant energy consumption and makes difficult the dimensional control of the resulting product.

SUMMARY OF THE INVENTION

[0004] The present invention provides shape memory alloys comprising:

(a) an effective amount of Mn, preferably at least about 18%;

(b) an effective amount of Si, preferably at least about 5%;

(c) from about 1% to about 8% Cr;

(d) an effective amount, preferably greater than about 0.08%, of N; and

(e) the balance of Fe.

Preferably, the alloys comprise from about 20% to about 30% Mn, from about 5.5% to about 6% of Si, from about 2% to about 5% of Cr, from about 0.1% to about 0.5% N, and from about 61% to about 70% Fe. Preferred embodiments demonstrate about 100% shape recovery with one cycle of thermo-mechanical training with a prestrain of about 3%. Methods for training the alloys are provided, comprising the steps of

(a) tensile deforming said alloy by applying from about 2.5% to about 4% prestrain at ambient temperature, preferably from about 4°C to about 45° C;

(b) heating said alloy to a temperature of from about 500°C to about 700°C for at least about 2 minutes; and

(c) cooling said alloy.

[0005] It has been found that alloys of this invention afford benefits over alloys among those known in the art. Such benefits include good resistance to corrosion, 100 percent shape recovery after as few as one cycle of training, and economical production.

DESCRIPTION OF THE INVENTION

[0006] The present invention provides iron-manganese-silicon-based shape memory alloy containing Cr (chromium) and N (nitrogen). In particular, the present invention provides an improved iron-manganese-silicon-based shape memory alloy, the improvement comprising the addition to said alloy of from about 1% to about 8% Cr; and from about 0.08% to about 0.5% N. Preferably, the iron-manganese-silicon-based shape memory alloy of comprises from about 18% to about 35% Mn (manganese); from about 5% to about 8% Si (silicon); and from about 55% to about 75% Fe (iron). More preferably, the alloy comprises from about 20% to about 30% Mn; from about 5.5% to about 6% Si; from about 55% to about 75% Fe; from about 2% to about 5% of Cr; and from about 0.1 % to about 0.4% N. (As used herein, the words "preferred" and "preferably" refer to embodiments of the invention that afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful and is not intended to exclude other embodiments from the scope of the invention.)

[0007] In general, and without being bound by theory, the shape memory mechanism of iron-based shape memory alloys results from the γ(fcc) $\rightarrow$ ε(hcp) stress-induced martensitic phase transformation generated by partial dislocation slipping and its reverse transformation. According to the prior art on shape memory mechanisms, Fe-Mn-Si based alloys have very low stacking fault energy (about mJ/m^2 order of magnitude). Therefore, on the $\{111\}_{fcc}$ planes, ½ <110> perfect dislocation dissociates into two 1/6 <112> partial dislocations, between which there is a stacking fault. In this type of alloy, ε (hcp) martensite can form every other layer of the {111} planes through these Shockley partial imperfect dislocation slips and through fault extension and stacking. This phase transformation can occur when the alloy is quenched from austenitic state hardening to temperatures lower than M_s (about 0°C, for example), i.e. the so-called thermally-induced martensite (TIM) phase transformation. Phase transformation can also occur when there is deformation at temperatures higher than M_s, but lower than M_d, i.e. so-called stress-induced martensite (SIM) phase transformation. The shape memory effect of this type of material is preferably realized through the second approach. The straining (or deformation) in austenitic state at room temperature generates SIM. Then it is heated to a temperature (about 600°C, for example) above A_f. Reverse transformation to an austenitic state results from the reverse movement (or slipping) of Shockley partial dislocations or the contraction of previously formed stacking faults. At the same time, the sample shape returns to its pre-deformation (austenite) state. The deformation process can be divided into three stages. The first stage is elastic deformation, the second stage is that in which ε martensitic phase transformation occurs, and the third stage will produce plastic deformation. Training can

raise the strength of parent austenite phase and increase the amount of reversible strain during the martensitic formation stage and thus improve the shape memory effect of the alloys. Alloying likewise can increase matrix strength and thereby magnify the effect of the martensite phase transformation stage.

[0008] A preferred alloy of the present invention comprises an effective amount, preferably at least about 18%, of Mn. An effective amount of Mn is that which allows formation of a shape memory alloy, preferably functioning as an austentite formation and stabilizing element. A preferred alloy comprises from about 20% to about 35%, more preferably from about 20% to about 30%, of Mn. A preferred alloy also comprises an effective amount, preferably at least about 5%, of Si. An effective amount of Si is that allows formation of a shape memory alloy, preferably functioning to improve the shape-memorizing characteristics of the alloy by acting on the austenite to raise its yield strength. A preferred alloy comprises from about 5.2% to about 8%, more preferably from about 5.5% to about 6%, of Si. A preferred alloy also comprises from about 1% to about 8% Cr, preferably from about 2% to about 5% of Cr. A preferred alloy also comprises an effective amount, preferably greater than about 0.08%, of N. An effective amount of N is that which allows formation of a shape memory alloy, preferably functioning to aid formation of austenite or improving corrosion resistance. A preferred alloy comprises from about 0.08% to about 5%, preferably from about 0.1% to about 0.4%, more preferably from about 0.1% to about 0.3%, of N. The balance of the alloy preferably comprises iron, preferably from about 55% to about 75%, more preferably from about 61% to about 70%, of iron.

[0009] A preferred embodiment consists essentially of: (a) from about 18% to about 35% of Mn; (b) from about 5% to about 8% of Si; (c) from about 1% to about 8% of Cr; (d) from about 0.08 % to about 0.5% N; and (e) the balance of Fe, wherein the alloy does not contain significant amounts of materials that degrade performance. Preferably, in such embodiments, the alloys do not contain significant amounts of C (carbon) or Ni (nickel).

The following alloy compositions are among those particularly preferred.

20% Mn, 5.5% Si, 5% Cr, 0.16% N, and the remainder Fe. Effectiveness: 3% prestrain, one training cycle, 100% shape recovery rate.

25% Mn, 5% Si, 5% Cr, 0.13% N, and the remainder Fe. Effectiveness: 3% prestrain, one training cycle, 100% shape recovery rate.

30% Mn, 6% Si, 2% Cr, 0.10% N, and the remainder Fe. Effectiveness: 3% prestrain, two training cycles, 100% shape recovery rate.

[0010] The present invention only requires a minimum number of training cycles to strengthen the parent austenitic matrix so as to increase the reversible strain and thereby improve the shape memory effect. Alloying with appropriate matrix-strengthening elements fundamentally improves the shape memory effect of the resulting alloy. The resulting alloy possesses superior shape memory features. In embodiments among those that are preferred, a 100% shape recovery rate is achieved after only one (or perhaps two, if the composition varies) thermomechanical training cycle in which a prestrain of from about 3.0% to about 3.5% is applied. In a preferred embodiment, the shape memory alloys of this invention demonstrate about 100% shape recovery with one cycle of thermo-mechanical training with a prestrain of about 3%. Also, in a preferred

embodiment, by adding an appropriate amount of Cr and N to an iron-based shape memory alloy having about 30% Mn, about 6% Si, and the remainder Fe, a new iron-based shape memory alloy is made in which the proportions are, preferably, from about 20% to about 30% Mn, from about 5% to about 6% Si, from about 2% to about 5% Cr, from about 0.10% to about 0.5% N, and the remainder Fe. This both improves the anti-corrosion properties of the alloy and makes possible a 100% shape recovery rate after just one or two training cycles. In a preferred embodiment training consists of tensile deforming an alloy by applying from about 3.0% to about 3.5% prestrain at room temperature, heating the alloy to approximately 600°C, and then cooling the alloy after keeping it at this temperature for about 10 minutes. If necessary, the aforesaid process can be repeated.

[0011] The present invention also provides methods of training an iron-manganese-silicon-based shape memory alloy containing Cr and N, comprising the steps of:

(a) tensile deforming said alloy by applying from about 2.5% to about 4% prestrain at a temperature of from about 4°C to about 45° C;

(b) heating said alloy to a temperature of from about 500°C to about 700°C for at least about 2 minutes; and

(c) cooling said alloy.

Preferably, the tensile deforming step comprises applying from about 3.0% to about 3.5% prestrain at ambient temperature. Also preferably, the heating step is for from about 5 minutes to about 15 minutes, at a temperature of from about 550°C to about 650°C. In a

preferred embodiment, the heating step is conducted for about 10 minutes at about 600°C. In another embodiment, the method additionally comprising repeating the training steps (a), (b), and (c), so that the training is performed two or three times.

[0012] The present invention possesses substantive characteristics and is a significant improvement over alloys among those in the art. Preferred embodiments of the alloys are inexpensive, highly strengthened, have good working qualities, and are highly corrosion resistant. Preferred embodiments can also achieve a 100% shape recovery rate after just one or two training cycles. Such alloys are suitable, for example, for manufacturing water and oil pipe couplings, fasteners, connectors, and other such parts, and have broad industrial and civil engineering applications. For example, water pipe couplings made from preferred alloys can withstand hydrostatic water pressure of up to 5 Mpa without leakage. With an improved design, they can withstand 50 Mpa and bear cyclic water pressures of 0-30 Mpa up to more than 500,000 times without leakage. The corrosion resistance and intergranular corrosion resistance in acidic and alkaline media of preferred alloys are superior to stainless steel.